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MECHANISMS OF CO2 REDUCTION ON METAL AND MODIFIED
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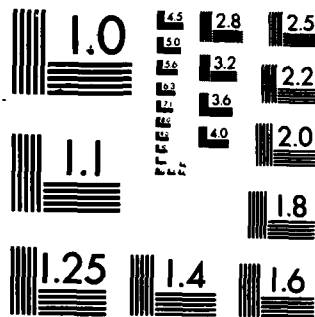
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October 21, 1986

Annual Report
For the Period January 1, 1986 to October 1, 1986

MECHANISMS OF CO₂ REDUCTION ON METAL AND
MODIFIED SEMICONDUCTOR ELECTRODES

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ONR Contract No. N000 14-86-C-0121
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Part I

October 1, 1986

ONR Contract N000 14-86-C-0121
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Papers Submitted:

1. K. W. Frese, Jr., Calculation of Binding Energies of H, O, and C atoms on Metal Surfaces. Surface Science.
2. K. W. Frese, Jr., Application of the Polar Covalence Model to Bonding and Energetics of CO Adsorption on Metal Surfaces. Applications of Surface Science.

Book Manuscripts Submitted:

1. Chapter entitled "GaAs." K. W. Frese, Jr., in Semiconductor Electrodes, H. O. Finklea (ed). Plenum Press (1987).
2. American Chemical Society Symposium Volume, The Catalytic Activation of CO₂. K. W. Frese, Jr., and D. P. Summers, "The Electrochemical Reduction of Aqueous Carbon Dioxide at Electroplated Ru Electrodes. Investigations Toward the Mechanism of Methane Formation." (1987). Partial Support by the Gas Research Institute.

Invited Presentation

1. American Chemical Society Symposium on The Catalytic Activation of Carbon Dioxide. New York, N.Y., April 1986. Partial support by the Gas Research Institute.

* Initial 9-mos period of contract.



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Part II

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Cognizant ONR Scientific Officer: Dr. Harold E. Guard

Project Description

The goal of this project is to elucidate the mechanism of the electrochemical reduction of CO_2 to methanol. A number of materials have been identified that form methanol in an electrochemical cell. These are GaAs, InP, Mo, W, and Ru. These electrode materials are used to determine the reaction mechanism. It has been shown that chemical steps limit the rate of CO_2 reduction on GaAs, and therefore, the extent of surface chemical reactions and their role in the formation of methanol are of great interest.

We are using a two-fold approach to mechanistic determination. First, elementary steps in the mechanism are postulated and then the thermodynamics of these steps is evaluated. The calculations allow us to: 1) reject steps with unfavorable energetics, 2) aid in the calculation of rates of feasible steps, and 3) obtain a global view of the probability of certain steps on a wide variety of materials.

To predict surface reaction energetics, we need a reliable simple model of surface chemical binding. A semi-empirical model of bond energies that has been shown to be remarkably accurate for molecules and bulk solids is the Polar Covalence Model developed by R. T. Sanderson. We have been successfully proving the value of this model for calculation of binding energetics of atoms and simple molecules. The model is validated using the experimental data on heats of chemisorption of hydrogen, oxygen, carbon, carbon monoxide and carbon dioxide.

The experimental phase of this study includes electrochemical kinetic measurements on the CO_2 reduction reaction. Essential data to be acquired include rates of product formation and faradaic efficiencies as a function of electrode potential, and pH. In addition, we are

attempting to observe surface-bound reaction intermediates. Computer data acquisition and manipulation of fast voltage transient data and FTIR are being employed. Identification of intermediates will suggest a rate limiting step and the results will be compared with model calculations.

Significant Results

The Polar Covalence Model developed by R. T. Sanderson was used to calculate binding energies at zero coverage for H, O, and C atoms adsorbed on metal surfaces. For 11 single-crystal metals, the average absolute difference between the experimental and calculated binding energies of hydrogen atoms was 3 to 4 kcal mol⁻¹. The model correctly predicts the weak binding of H on sp metals, eg., Hg and Cd. Very similar agreement, 3 to 4 kcal mol⁻¹, was obtained for O atoms on 8 single-crystal metals. In the case of carbon atoms, the binding energy on Ru and Ni was calculated to be less than the atomization energy of graphite, in agreement with experiment. A similar effect on Pd surfaces is predicted. The calculated low binding energy, 40 kcal mol⁻¹, of H atoms on top of Pd is supported by a combination of thermodynamic, quantum mechanical, spectroscopic, and thermal desorption data. These calculations represent the first attempt to apply Sanderson's method to first, second, and third row transition metals and to surface thermodynamics.

The Polar Covalence Model was also used to calculate zero coverage heats of chemisorption of CO on metal surfaces. The goals of this work are to establish the predictive power of the approach and to eventually obtain heats of surface chemical reactions. Chemisorption heats were calculated for five stereochemical possibilities including single and double bonded linear CO, bridge bonded, sideways bonded and dissociated CO on fifteen first, second, and third row transition metals. The role of surface steps, other defects, and CO-CO interactions were not considered. Very good agreement, less than 3 kcal mol⁻¹ difference between experiment and calculation, was observed for Mn, Ni, Co, Rh, Pd, W, Re, Ir, and Pt. For Cu, Ag, and Ru, experiment and model calculations

differed by 4 to 5 kcal mol⁻¹. In the complicated case of W, three of four CO desorption peaks were assigned to two linear types of CO and the bridge-bonded CO. The basis of the assignment was the agreement within experimental error between the calculations and the known desorption spectrum. The heat of desorption from the dissociated state on W was also satisfactorily calculated. The heat of direct dissociation for the recently controversial case of CO on Rh is calculated to be +19 kcal mol⁻¹. CO dissociation is also clearly predicted to be forbidden on Pd, Ag, and Pt. Endothermic heats of dissociative chemisorption of 1 to 8 kcal mol⁻¹ were calculated for Ru, Mo, Re, and Ir, suggesting little tendency for dissociation for these metals under high vacuum conditions.

In the laboratory, we assembled a computer-controlled data acquisition system for recording open circuit voltage transients. The system is composed of a 128K Apple II-e computer, an Applied Engineering 12-bit data acquisition card, and a simple auxiliary circuit that uses a IRF511 n-channel Si MOSFET as a current interrupter. The first data point is recorded at 30 μ s after current interrupt.

Some time was spent writing the assembly code needed to drive the card at the required speed. The system is currently being tested on real electrochemical systems, and the data acquisition program is working well.

Future Plans

The validity of the Polar Covalence Model has been proven in our first two technical reports. The next step will be to apply the model to heats of chemisorption of CO₂ from the gas phase. Then we will be ready to investigate the thermodynamics of the possible elementary steps in the electrochemical CO₂ reduction. The initial step to be investigated will be the reaction of dissolved CO₂ with adsorbed hydrogen atoms to give adsorbed formate radicals. The results will be compared with direct electron transfer to CO₂ with cooperation of a solvated proton. These steps are the most likely to be operative in CO₂ reduction. The calculations will include transition and sp metals. We will proceed

systematically to the next stage of the reduction process, which might lead to either formic acid, CO, or formyl radicals. In addition to the thermodynamics, the rates of the individual steps will be considered on each material. For example, the Marcus theory, which takes bonding of intermediates into account, will be used to estimate rates of the electron transfer steps. The rates of chemical steps will be calculated using transition state theory and the Marcus model using bond force constants for adsorbed species.

The experimental phase of the work will focus on detection of intermediates with electrodes already known to form methanol. The use of voltage transients to quantify overpotential adsorbed intermediates has been promoted by B. Conway. We have built a similar capability in our laboratory as described above; we will apply the method to CO₂ reduction chemistry.

We will be making our first attempts at FTIR spectroscopy on electrode surfaces in the coming year. The goal of this task is also to detect and identify adsorbed intermediates.

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